

PATENT ABSTRACTS OF JAPAN

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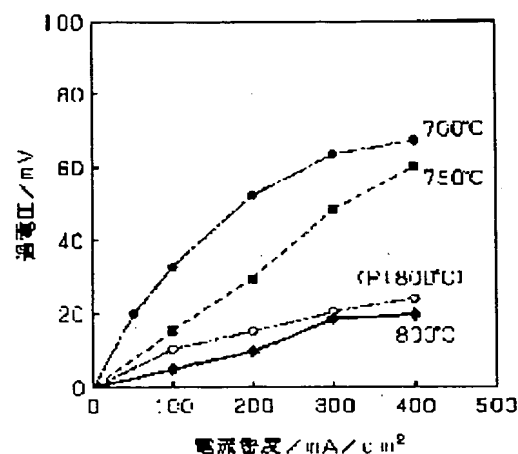
(54) OXIDATION ELECTRODE FOR OXIDE SOLID ELECTROLYTE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an electrode having a long service life and an excellent function that is used for such an electrochemical device and a sensor as a solid electrolyte type fuel cell, using a solid electrolyte of a perovskite-type oxide containing barium, taking most advantage of the electrolyte property.

SOLUTION: An oxidation electrode for an oxide solid electrolyte composed of a perovskite-type oxide containing barium and a rare earth metal element, barium and lanthanum, and a perovskite oxide containing Mn, Fe, Co, Ni, Cu, is used.

本発明の Ba_{0.8}Ba_{0.4}Co_{0.8}酸化物の
各種温度での運転電圧



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CLAIMS

[Claim(s)]

[Claim 1] The oxidation pole for oxide solid electrolytes characterized by consisting of perovskite mold oxide which contains Ba at least in the solid electrolyte of the perovskite mold oxide containing barium.

[Claim 2] The oxidation pole for oxide solid electrolytes characterized by a perovskite mold oxide according to claim 1 consisting of an ingredient which contains rare earth elements at least.

[Claim 3] Rare earth elements according to claim 2 are oxidation poles for oxide solid electrolytes characterized by including one of elements among Pr and Nd at least.

[Claim 4] The oxidation pole for oxide solid electrolytes characterized by consisting of perovskite mold oxide which contains Ba and La at least in the solid electrolyte of the perovskite mold oxide containing barium.

[Claim 5] The oxidation pole for oxide solid electrolytes characterized by a perovskite mold oxide according to claim 4 consisting of an ingredient which contains a kind of element at least among the elements of Mn, Fe, Co, nickel, and Cu.

[Claim 6] The oxidation pole for oxide solid electrolytes characterized by being the perovskite mold oxide of the presentation expressed with $Ba_{1-x}La_xMO_3$ (M is a trivalent cation) in the solid electrolyte of the perovskite mold oxide containing barium.

[Claim 7] It is an oxidation pole for the description and **** solid electrolytes about consisting of an ingredient with which M according to claim 6 contains at least one sort of elements among the elements of Mn, Fe, Co, nickel, and Cu.

[Claim 8] The oxidation pole for oxide solid electrolytes characterized by x according to claim 6 being 0.6.

[Claim 9] The oxidation pole for oxide solid electrolytes characterized by a perovskite mold oxide according to claim 6 being $Ba_{0.4}La_{0.6}CoO_3$.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the field using the solid electrolyte of the perovskite mold oxide containing especially barium about electrochemistry devices, such as a solid oxide fuel cell, and a sensor.

[0002]

[Description of the Prior Art] Oxides, such as the solid electrolyte O.2O_3 of the perovskite mold oxide containing barium, for example, $\text{BaCe}_{0.8}\text{Gd}$ etc., have high ion conductivity, and attract attention as a solid electrolyte which carries out electrical conduction also of the proton. In recent years, application of the various electrochemistry devices which used this kind of oxide for the solid electrolyte is considered, and, especially as for the application to a sensor or a fuel cell, expectation has started as what is replaced with the conventional zirconia system solid electrolyte.

[0003] However, the solid electrolyte of this system just began to attract attention recently, and is not proposed about the optimal electrode material for this kind, especially the oxidation pole in an elevated temperature. Current, platinum stable in reduction and an oxidizing atmosphere as an electrode in a standard elevated temperature, and noble metals, such as silver, are used.

[0004] On the other hand, as an oxidation pole of the zirconia mold fuel cell used at an elevated temperature, although PEROVSKITE mold oxides, such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$, are used When these are applied to the solid electrolyte of the perovskite mold oxide containing barium, an electrode material and a solid electrolyte react at an elevated temperature, generate the 2nd phase of a reaction, such as BaO and BaCoO_2 , and become the cause of degrading the property of a device, a cell, and a sensor.

[0005]

[Problem(s) to be Solved by the Invention] As above-mentioned, the optimal oxidation pole for the oxide solid electrolyte containing barium is not found out, with the electrode of platinum or silver, becomes cost quantity and is not suitable for utilization. Then, it did not react with a solid electrolyte at an elevated temperature, but it was long lasting and development of the electrode material of right conductivity which can pull out the electrolytic engine performance to the maximum extent was a technical problem.

[0006]

[Means for Solving the Problem] It is the oxidization pole characterized by this invention consisting of perovskite mold oxide which offers the oxidization pole for the solid electrolytes of the perovskite mold oxide containing barium in view of the above-mentioned technical problem, and specifically contains Ba, and perovskite mold oxide is desirably characterized by consisting of rare earth elements, especially an ingredient containing Pr and Nd at least.

[0007] Moreover, the above-mentioned technical problem is solved by offering the oxidation pole which is characterized by consisting of perovskite mold oxide which contains Ba and La at least, and is characterized by the perovskite mold oxide consisting of an ingredient which contains a kind of element at least among the elements of Mn, Fe, Co, nickel, and Cu desirably.

[0008] By performing the above-mentioned means, it does not react with the solid electrolyte of the perovskite mold oxide which contains barium by low cost, but it is long lasting and the highly efficient electrode which can pull out the electrolytic engine performance to the maximum extent can be obtained.

[0009]

[Embodiment of the Invention]

[0010]

[Example] Hereafter, the example of this invention is shown in a detail.

[0011] (Example 1) This example shows the example investigated about the reactivity of the ingredient of this invention, and the solid electrolyte of the perovskite mold oxide containing barium.

[0012] First, barium, the perovskite mold oxide and barium containing rare earth elements, and a lanthanum and the perovskite mold oxide which contains Mn, Fe, Co, nickel, and Cu further were compounded by the solid phase technique as an ingredient of this invention, and the planet ball mill etc. ground sintered compact powder to 1

micrometer or less. In the solid electrolyte containing these powder and barium, and this experiment, two sorts of solid electrolyte powder of the presentation which serves as $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$ $\text{BaZr}_{0.8}\text{In}_{0.2}\text{O}_3$ was mixed, and the reactivity was seen by heat-treating at 1200 degrees C for 10 hours. X diffraction measurement performed the presentation structure analysis before and behind heat treatment.

[0013] The result investigated about a presentation and reactivity of the oxidation pole compounded in this experiment, and a product is shown in (Table 1).

[0014]

[Table 1]

材 料	反 応 第 2 相
$\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	BaO
$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$	BaCoO_3
$\text{BaPr}_{0.6}\text{Gd}_{0.4}\text{O}_3$	なし
$\text{BaPr}_{0.6}\text{Gd}_{0.4}\text{O}_3$	なし
$\text{BaNd}_{0.6}\text{Gd}_{0.4}\text{O}_3$	なし
$\text{BaPm}_{0.6}\text{Gd}_{0.4}\text{O}_3$	なし
$\text{BaSm}_{0.6}\text{Gd}_{0.4}\text{O}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{MnO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{FeO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{NiO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{CuO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{Co}_{0.8}\text{Mn}_{0.2}\text{O}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{Co}_{0.8}\text{Mn}_{0.2}\text{O}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{Sr}_{0.1}\text{CoO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{Ca}_{0.1}\text{CoO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{Sr}_{0.1}\text{Co}_{0.8}\text{Mn}_{0.2}\text{O}_3$	なし

[0015] (Table 1) showed that barium, the perovskite mold oxide and barium containing rare earth elements, and a lanthanum and the perovskite mold oxide which contains Mn, Fe, Co, nickel, and Cu further hardly reacted with the solid electrolyte of the perovskite mold oxide containing barium.

[0016] (Example 2) This example can be applied and burned on the solid electrolyte of the perovskite mold oxide containing barium, carries out the ingredient of this invention, and investigates the electrode engine performance.

[0017] First, after it compounded the oxidization pole which is this invention like a last example by the solid phase technique and the planet ball mill ground, it pasted. The paste added the 4wt(s)% polyvinyl butyral to the powdered raw material as binding material, and mixed and adjusted it into the mixed solvent of ethanol and toluene. In the solid electrolyte of the perovskite mold oxide containing barium, and this experiment, this paste was applied on the discoid (0.5tx13phi) sample of the solid electrolyte of the presentation which becomes $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$, it carried out by the ability having been burned at 1200 degrees C among air, and the test portion was produced.

[0018] In addition, it could be burned on the counter electrode and Pt electrode was used. Pt reference pole was established in the cel, the overvoltage of an oxidation pole was measured, and the engine performance of an electrode was evaluated.

[0019] The overvoltage measurement result in the various temperature at the time of using the $\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$

oxidation pole of this invention for drawing 1 is shown. Moreover (Table 2), the overvoltage at the time of 200 mA/cm² energization of the oxidation pole produced in this experiment is shown. Also when Pt is used for an oxidation pole for a comparison, it is shown collectively.

[0020]

[Table 2]

酸化極の200mA/cm²通電時の過電圧 (m V)

材 料	8 0 0 °C	7 5 0 °C	7 0 0 °C
Pt	1 5	3 8	6 0
La _{0.1} Sr _{0.1} MnO ₃	1 2	3 1	5 5
La _{0.1} Sr _{0.1} CoO ₃	1 0	2 8	4 8
BaPr _{0.1} Gd _{0.1} O ₃	4 5	1 2 5	2 0 2
BaPr _{0.1} Gd _{0.1} O ₃	4 1	1 0 5	1 9 0
BaNd _{0.1} Gd _{0.1} O ₃	4 6	1 3 8	2 3 1
BaPm _{0.1} Gd _{0.1} O ₃	4 4	1 3 1	2 2 0
BaSm _{0.1} Gd _{0.1} O ₃	5 1	1 5 6	2 9 7
La _{0.1} (Ba) _{0.1} (MnO ₃	1 3	3 2	5 5
La _{0.1} (Ba) _{0.1} (FeO ₃	1 4	3 3	5 6
La _{0.1} (Ba) _{0.1} (CoO ₃	1 0	3 0	5 2
La _{0.1} (Ba) _{0.1} (NiO ₃	1 1	3 1	5 2
La _{0.1} (Ba) _{0.1} (CuO ₃	1 3	3 5	6 1
La _{0.1} (Ba) _{0.1} (CoO ₃	1 1	3 4	6 0
La _{0.1} (Ba) _{0.1} (CoO ₃	1 2	3 8	6 9
La _{0.1} (Ba) _{0.1} (Co _{0.1} Mn _{0.1} O ₃	1 1	3 1	5 3
La _{0.1} (Ba) _{0.1} (Co _{0.1} Mn _{0.1} O ₃	1 2	3 2	5 4
La _{0.1} (Ba) _{0.1} (Sr _{0.1} CoO ₃	1 0	3 1	5 0
La _{0.1} (Ba) _{0.1} (Ca _{0.1} CoO ₃	1 3	3 4	6 2
La _{0.1} (Ba) _{0.1} (Sr _{0.1} Co _{0.1} Mn _{0.1} O ₃	1 2	3 3	5 5

[0021] As shown in (Table 2), the perovskite mold oxide containing barium and rare earth elements especially barium, and a lanthanum and the perovskite mold oxide which contains Mn, Fe, Co, nickel, and Cu further are understood that an overvoltage is comparatively small comparable as Pt. It is thought that the oxidation pole of this invention is pulling out the electrolytic engine performance enough like the conventional platinum electrode.

[0022] The ingredient of this invention has the temperature characteristic, respectively, and can choose the optimal ingredient with electrolytic service temperature. By using the ingredient of this invention from the above thing, it was proved that the electrolytic engine performance could be conventionally pulled out by low cost the conventional platinum electrode and more than comparable.

[0023] (Example 3) This example is an example the highly efficient fuel cell at the time of applying the oxidation pole of this invention to the air pole of a solid oxide fuel cell is proved [example].

[0024] As shown in drawing 2 , BaCe_{0.8}Gd_{0.2}O_{3-a} (0.50mm in thickness) was used as an air pole 1 as a solid electrolyte 2 of the perovskite mold oxide which contains barium for oxidization pole ingredient La_{0.6}Ba_{0.4}CoO₃ of this invention, nickel cermet was used as a fuel electrode 3, the small fuel cell cel was produced, air 4 and hydrogen 5 were supplied to each pole, and the fuel cell was made to operate. In addition, as for gas packing and 7, as for a lead and 8, 6 is an outer tube.

[0025] The air of 200 ml/min was supplied to the air pole, it carried out by having supplied the humidification hydrogen of 200 ml/min to the fuel electrode at 800 degrees C, and the spark test and the continuous discharge trial by 100 mA/cm² were performed. At the spark test, the good discharge property of 0.2 W/cm² was shown by 0.5mm in 800 degrees C and electrolyte thickness, by the continuous discharge trial by 100 mA/cm², it was

able to discharge to stability for 1000 hours, and the electrical-potential-difference change was able to obtain the very good result about 1%/1000h. High performance and a long lasting fuel cell can be obtained by low cost from the conventional electrode by there being less electrical-potential-difference rate of change in a continuous discharge property than Pt, and using the ingredient of this invention mostly efficiently, as compared with the cell which consisted of conventional Pt(s) from this, above equivalent.

[0026] In addition, although this example showed the example using $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\alpha}$ as a solid electrolyte of the perovskite mold oxide containing barium, $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\alpha}$, $\text{BaZr}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\alpha}$, etc. are sufficient as a solid electrolyte, and if it is a perovskite mold oxide containing Ba, it is good anything.

[0027] Moreover, although this example showed focusing on the example which used $\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$ as an oxidation pole ingredient, if the configuration element is contained, the thing of the presentation of those other than these is also easy to be natural [the ingredient indicated not only in this but in (the table 1) is sufficient, and]. Of course, in a metal condition or an oxide condition is sufficient as a start raw material, and the method of preparation of an ingredient and a synthesis method do not specify a synthesis method with a solid phase technique, a gaseous-phase method, or a solution method, either.

[0028] Moreover, the structure of an electrode etc. is not specified. In this example, although the example of a 800-degree C fuel cell was shown, it is applicable to sensors, electrochemistry devices, etc. other than a fuel cell.

[0029]

[Effect of the Invention] This invention can obtain the long lasting and highly efficient electrode which is low cost and can pull out the electrolytic engine performance to the maximum extent by offering barium, the perovskite mold oxide and barium containing rare earth elements, and a lanthanum and the perovskite mold oxide which contains Mn, Fe, Co, nickel, and Cu further as an oxidization pole for the solid electrolytes of the perovskite mold oxide containing barium.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing of the overvoltage in the various temperature of the $\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$ oxidation pole of this invention

[Drawing 2] Drawing of a fuel cell using the oxidation pole of this invention

[Description of Notations]

- 1 Air Pole
- 2 Solid Electrolyte
- 3 Fuel Electrode
- 4 Air
- 5 Hydrogen
- 6 Gas Packing
- 7 Lead
- 8 Outer Tube

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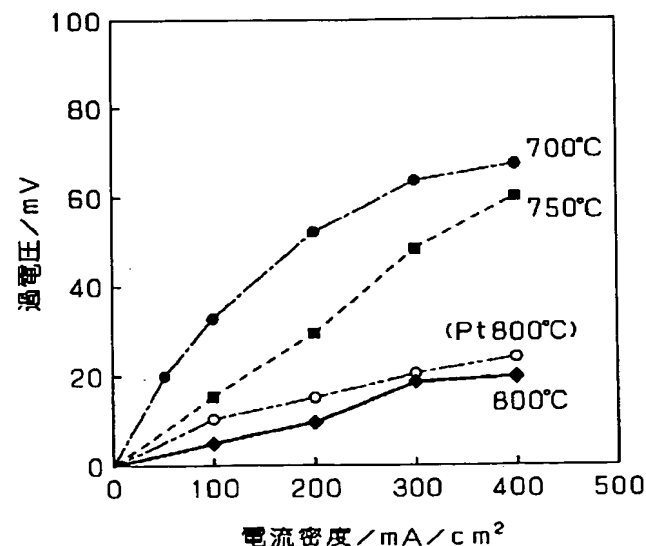
(54)【発明の名称】 酸化物固体電解質用の酸化極

(57)【要約】

【課題】 バリウムを含むペロブスカイト型酸化物の固体電解質を用いた固体電解質型燃料電池などの電気化学デバイス、センサーにおいて、低コストで、かつ電解質の性能を最大限に引き出せる長寿命、高性能な電極が必要であった。

【解決手段】 バリウムと希土類元素を含むペロブスカイト型酸化物、バリウムとランタン、さらにMn、Fe、Co、Ni、Cuを含むペロブスカイト型酸化物の材料からなる酸化物固体電解質用の酸化極を用いる。

本発明の $\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$ 酸化極の
各種温度での過電圧



【特許請求の範囲】

【請求項1】 バリウムを含むペロブスカイト型酸化物の固体電解質において、少なくともBaを含むペロブスカイト型酸化物からなることを特徴とする酸化物固体電解質用の酸化極。

【請求項2】 請求項1に記載のペロブスカイト型酸化物が少なくとも希土類元素を含む材料からなることを特徴とする酸化物固体電解質用の酸化極。

【請求項3】 請求項2に記載の希土類元素は少なくともPr、Ndのいずれかの元素を含むことを特徴とする酸化物固体電解質用の酸化極。

【請求項4】 バリウムを含むペロブスカイト型酸化物の固体電解質において、少なくともBaとLaを含むペロブスカイト型酸化物からなることを特徴とする酸化物固体電解質用の酸化極。

【請求項5】 請求項4に記載のペロブスカイト型酸化物がMn、Fe、Co、Ni、Cuの元素の内少なくとも一種の元素を含む材料からなることを特徴とする酸化物固体電解質用の酸化極。

【請求項6】 バリウムを含むペロブスカイト型酸化物の固体電解質において $Ba_{1-x}La_xMO_3$ (Mは3価のカチオン) で現される組成のペロブスカイト型酸化物であることを特徴とする酸化物固体電解質用の酸化極。

【請求項7】 請求項6に記載のMがMn、Fe、Co、Ni、Cuの元素の内少なくとも1種の元素を含む材料からなることを特徴とする酸化物固体電解質用の酸化極。

【請求項8】 請求項6に記載のxが0.6であることを特徴とする酸化物固体電解質用の酸化極。

【請求項9】 請求項6に記載のペロブスカイト型酸化物が $Ba_{0.4}La_{0.6}CoO_3$ であることを特徴とする酸化物固体電解質用の酸化極。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、固体電解質型燃料電池などの電気化学デバイス、センサーに関するもので、特にバリウムを含むペロブスカイト型酸化物の固体電解質を用いる分野に関するものである。

【0002】

【従来の技術】バリウムを含むペロブスカイト型酸化物の固体電解質、例えば $BaCe_{0.8}Gd_{0.2}O_3$ などの酸化物は、高いイオン導電性を有し、プロトンも電導する固体電解質として注目されている。近年、この種の酸化物を固体電解質に用いた各種電気化学デバイスの応用が検討されており、特にセンサーや燃料電池への応用は従来のジルコニア系固体電解質に取って代わるものとして期待がかかっている。

【0003】しかしながらこの系の固体電解質は最近注目され始めたところであり、この種に最適の電極材料、特に高温での酸化極については提案されていない。現

在、標準的な高温での電極として還元・酸化雰囲気中で安定な白金や、銀などの貴金属が使用されている。

【0004】一方、高温で用いられるジルコニア型燃料電池の酸化極として、 $La_{1-x}Sr_xMnO_3$ 、 $La_{1-x}Sr_xCoO_3$ や $La_{1-x}Ca_xCoO_3$ などのペロブスカイト型酸化物が用いられているが、バリウムを含むペロブスカイト型酸化物の固体電解質にこれらを適用した場合、電極材料と固体電解質が高温で反応し、 BaO や $BaCO_2$ などの反応第2相を生成し、デバイスや電池、センサの特性を劣化させる原因となる。

【0005】

【発明が解決しようとする課題】前述の通り、バリウムを含む酸化物固体電解質に最適の酸化極は見いだされておらず、白金や銀の電極ではコスト高になり実用化には適さない。そこで、高温で固体電解質と反応せず長寿命で、かつ電解質の性能を最大限に引き出せる良電導性の電極材料の開発が課題であった。

【0006】

【課題を解決するための手段】本発明は、上記課題に鑑み、バリウムを含むペロブスカイト型酸化物の固体電解質用の酸化極を提供するものであり、具体的にはBaを含むペロブスカイト型酸化物からなることを特徴とする酸化極であり、望ましくはペロブスカイト型酸化物が少なくとも希土類元素、特にPr、Ndを含む材料からなることを特徴とする。

【0007】また、少なくともBaとLaを含むペロブスカイト型酸化物からなることを特徴とし、望ましくは、そのペロブスカイト型酸化物がMn、Fe、Co、Ni、Cuの元素の内少なくとも一種の元素を含む材料からなることを特徴とする酸化極を提供することにより上記課題を解決するものである。

【0008】上記手段を実行することにより、低コストでバリウムを含むペロブスカイト型酸化物の固体電解質と反応せず長寿命で、かつ電解質の性能を最大限に引き出せる高性能な電極を得ることができる。

【0009】

【発明の実施の形態】

【0010】

【実施例】以下、本発明の実施例について詳細に示す。

【0011】(実施例1)本実施例は本発明の材料とバリウムを含むペロブスカイト型酸化物の固体電解質との反応性について調べた事例を示す。

【0012】まず、本発明の材料としてバリウムと希土類元素を含むペロブスカイト型酸化物、バリウムとランタン、さらにMn、Fe、Co、Ni、Cuを含むペロブスカイト型酸化物を固相法により合成し、焼結体粉末を遊星ボールミル等で1μm以下に粉碎した。これらの粉末とバリウムを含む固体電解質、本実験では $BaCe_{0.8}Gd_{0.2}O_3$ と $BaZr_{0.8}In_{0.2}O_3$ なる組成の2種の固体電解質粉末を混合し、1200℃で、10時間熱処理すること

によりその反応性を見た。熱処理前後の組成構造分析はX線回折測定により行った。

【0013】(表1)に本実験で合成した酸化極の組成*

*と反応性、生成物について調べた結果を示す。

【0014】

【表1】

材 料	反 応 第 2 相
$\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	BaO
$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$	BaCoO_3
$\text{BaPr}_{0.4}\text{Gd}_{0.2}\text{O}_3$	なし
$\text{BaPr}_{0.4}\text{Gd}_{0.1}\text{O}_3$	なし
$\text{BaNd}_{0.4}\text{Gd}_{0.1}\text{O}_3$	なし
$\text{BaPm}_{0.4}\text{Gd}_{0.1}\text{O}_3$	なし
$\text{BaSm}_{0.4}\text{Gd}_{0.1}\text{O}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{MnO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{FeO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{NiO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{CuO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{Co}_{0.8}\text{Mn}_{0.2}\text{O}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{Co}_{0.8}\text{Mn}_{0.2}\text{O}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{Sr}_{0.1}\text{CoO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{Ca}_{0.1}\text{CoO}_3$	なし
$\text{La}_{0.6}\text{Ba}_{0.4}\text{Sr}_{0.1}\text{Co}_{0.8}\text{Mn}_{0.2}\text{O}_3$	なし

【0015】(表1)より、バリウムと希土類元素を含むペロブスカイト型酸化物、バリウムとランタン、さらにMn、Fe、Co、Ni、Cuを含むペロブスカイト型酸化物は、バリウムを含むペロブスカイト型酸化物の固体電解質とほとんど反応しないことがわかった。

【0016】(実施例2)本実施例は本発明の材料をバリウムを含むペロブスカイト型酸化物の固体電解質に塗布、焼き付けし電極性能を調べたものである。

【0017】まず、前実施例と同様に本発明である酸化極を固相法により合成し、遊星ボールミルで粉碎した後、ペースト化した。ペーストは、粉末の原材料に結着材として4wt%のポリビニルブチラールを加えエタノールとトルエンの混合溶媒中に混合し調整した。バリウムを含むペロブスカイト型酸化物の固体電解質、本実験

では、 $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$ なる組成の固体電解質の円盤状(0.5t×13φ)試料上にこのペーストを塗布し、空气中1200℃で焼き付けして測定試料を作製した。

【0018】なお、対極に焼き付けPt電極を用いた。セルにはPt参照極を設けて酸化極の過電圧を測定し電極の性能を評価した。

【0019】図1に本発明の $\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$ 酸化極を用いた場合の各種温度での過電圧測定結果を示す。また(表2)に本実験で作製した酸化極の200mA/cm²通電時の過電圧を示す。比較のために酸化極にPtを用いた場合も併せて示す。

【0020】

【表2】

酸化極の200mA/cm²通電時の過電圧 (mV)

材 料	8 0 0 ℃	7 5 0 ℃	7 0 0 ℃
Pt	1 5	3 8	6 0
La _{0.1} Sr _{0.1} MnO ₃	1 2	3 1	5 5
La _{0.1} Sr _{0.1} CoO ₃	1 0	2 8	4 8
BaPr _{0.8} Gd _{0.1} O ₃	4 5	1 2 5	2 0 2
BaPr _{0.8} Gd _{0.1} O ₃	4 1	1 0 5	1 9 0
BaNd _{0.8} Gd _{0.1} O ₃	4 6	1 3 8	2 3 1
BaPm _{0.8} Gd _{0.1} O ₃	4 4	1 3 1	2 2 0
BaSm _{0.8} Gd _{0.1} O ₃	5 1	1 5 6	2 9 7
La _{0.1} Ba _{0.1} MnO ₃	1 3	3 2	5 5
La _{0.1} Ba _{0.1} FeO ₃	1 4	3 3	5 6
La _{0.1} Ba _{0.1} CoO ₃	1 0	3 0	5 2
La _{0.1} Ba _{0.1} NiO ₃	1 1	3 1	5 2
La _{0.1} Ba _{0.1} CuO ₃	1 3	3 5	6 1
La _{0.1} Ba _{0.1} CoO ₃	1 1	3 4	6 0
La _{0.1} Ba _{0.1} CoO ₃	1 2	3 8	6 9
La _{0.1} Ba _{0.1} Co _{0.8} Mn _{0.1} O ₃	1 1	3 1	5 3
La _{0.1} Ba _{0.1} Co _{0.8} Mn _{0.1} O ₃	1 2	3 2	5 4
La _{0.1} Ba _{0.1} Sr _{0.1} CoO ₃	1 0	3 1	5 0
La _{0.1} Ba _{0.1} Ca _{0.1} CoO ₃	1 3	3 4	6 2
La _{0.1} Ba _{0.1} Sr _{0.1} Co _{0.8} Mn _{0.1} O ₃	1 2	3 3	5 5

【0021】(表2)に示すように、バリウムと希土類元素を含むペロブスカイト型酸化物、特にバリウムとランタン、さらにMn、Fe、Co、Ni、Cuを含むペロブスカイト型酸化物は、過電圧が比較的小さくPtと同程度であることがわかる。本発明の酸化極は従来の白金電極と同様に充分電解質の性能を引き出しているものと考えられる。

【0022】本発明の材料は、それぞれ温度特性を持っており、電解質の使用温度により最適の材料を選ぶことが出来る。以上のことより本発明の材料を用いることにより、従来より低コストで電解質の性能を従来の白金電極と同程度以上に引き出すことが出来ることが実証された。

【0023】(実施例3)本実施例は、本発明の酸化極を固体電解質型燃料電池の空気極に適用した場合の高性能な燃料電池を実証する事例である。

【0024】図2に示すように空気極1として本発明の

酸化極材料La_{0.6}Ba_{0.4}CoO₃を、バリウムを含むペロブスカイト型酸化物の固体電解質2としてBaCe_{0.8}Gd_{0.2}O_{3-δ}(厚さ0.50mm)を、燃料極3としてNiサメットを用いて小型燃料電池セルを作製し、各々の極に空気4および水素5を供給して燃料電池を運転させた。なお、6がガスパッキン、7はリード、8は外管である。

40 【0025】800℃で空気極に200ml/minの空気を、燃料極に200ml/minの加湿水素を供給し行い、放電試験および100mA/cm²での連続放電試験を行った。放電試験では、800℃、電解質厚さ0.5mmで、0.2W/cm²の良好な放電特性を示し、100mA/cm²での連続放電試験では、1000時間安定に放電し、その電圧変化は1%/1000h程度で極めて良好な結果を得ることができた。このことより従来のPtで構成された電池と比較して性能的にほぼ同等以上で、連続放電特性での電圧変化率はPtより
50 少なく、本発明の材料を用いることにより、従来の電極

より低コストで高性能、長寿命な燃料電池を得ることができる。

【0026】なお、本実施例ではバリウムを含むペロブスカイト型酸化物の固体電解質として $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ を用いた事例を示したが、固体電解質として $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ や $\text{BaZr}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ 、などでも良いし、Baを含むペロブスカイト型酸化物であれば何でも良い。

【0027】また、本実施例では、酸化極材料として $\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$ を用いた事例を中心に示したが、これに限らず（表1）に記載されている材料でも良いし、構成元素が含まれていればこれら以外の組成のものでももちろん良い。もちろん、材料の調製法、合成法は、出発原料が金属状態でも、酸化物状態でも良いし、合成法も固相法でも、気相法でも溶液法でも規定するものではない。

【0028】また、電極の構造など規定するものではない。本実施例では、800℃での燃料電池の事例を示したが、燃料電池以外のセンサや電気化学デバイスなどにも適用可能である。

【0029】

【発明の効果】本発明は、バリウムを含むペロブスカイ

ト型酸化物の固体電解質用の酸化極として、バリウムと希土類元素を含むペロブスカイト型酸化物、バリウムとランタン、さらにMn、Fe、Co、Ni、Cuを含むペロブスカイト型酸化物を提供することにより、低コストでかつ電解質の性能を最大限に引き出せる長寿命、高性能な電極を得ることができる。

【図面の簡単な説明】

【図1】本発明の $\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$ 酸化極の各種温度での過電圧の図

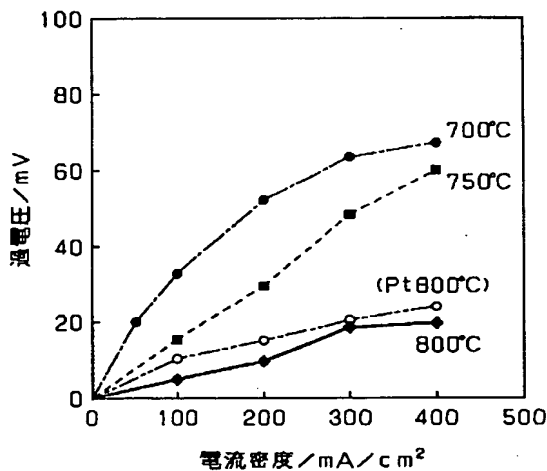
10 【図2】本発明の酸化極を用いた燃料電池の図

【符号の説明】

- 1 空気極
- 2 固体電解質
- 3 燃料極
- 4 空気
- 5 水素
- 6 ガスパッキン
- 7 リード
- 8 外管

【図1】

本発明の $\text{La}_{0.6}\text{Ba}_{0.4}\text{CoO}_3$ 酸化極の
各種温度での過電圧



【図2】

本発明の酸化極を用いた燃料電池

